

synchronous decarboxylation and dehydration reaction which is characteristic of the hydroxy acid.

A more detailed consideration of these results is now in order. For the decarboxylation of β -phenylcinnamic acid eq. 3 is more properly replaced by eq. 7 where

$$k_{\text{obsd}} = \frac{k_1(h_0)^\alpha k_3(h_0)^\gamma}{k_2(h_0)^\beta + k_3(h_0)^\gamma} \quad (7)$$

associated with each of the steps k_1 , k_2 , and k_3 is a dependency on the acidity of the medium, h_0^α , h_0^β , and h_0^γ , respectively. For the present situation γ is less than β and eq. 7 can be simplified to eq. 8, a form in which it is easier to envisage the result to be expected.

$$k_{\text{obsd}} = \frac{k_1(h_0)^\alpha k_3}{k_2(h_0)^{\beta-\gamma} + k_3} \quad (8)$$

From eq. 8 it is apparent that k_{obsd} reduces to $k_1(H^+)^\alpha$ when the acid concentration is very low (*i.e.*, $k_2(H^+)^{\beta-\gamma} \ll k_3$).

This then results in a simple, acid-catalyzed behavior in regions of low acid concentration, completely in accord with the observations. In the region of 20–40% sulfuric acid the decarboxylation of β -phenylcinnamic acid shows a particularly simple form and a plot of $\log k_{\text{obsd}}$ vs. H_0 is linear and of unit slope. Hence α is 1.

At the extreme of high sulfuric acid concentration eq. 8 reduces to eq. 9.

$$k_{\text{obsd}} = (k_1/k_2)k_3(h_0)^{\alpha-\beta+\gamma} \quad (9)$$

Substituting for k_1/k_2 an equilibrium constant for step 1 (eq. 1) gives eq. 10, which of course is a familiar

$$k_{\text{obsd}} = K_{\text{eq}}k_3(h_0)^{\alpha-\beta+\gamma} \quad (10)$$

result for a pre-equilibrium followed by a rate-limiting step. Noteworthy in this instance, however, is the complex of acid catalysis terms which accumulate. Equation 10 results in a linear plot when the observed rate is plotted against H_0 , but the slope of such a plot is a composite of the acid dependency of each of the three steps. As α is known to be 1, and β and γ have been determined independently as 1.14 and 0.5, respectively, eq. 10 predicts a limiting slope (in very high concentrations of sulfuric acid) for the decarboxylation of β -phenylcinnamic acid of 0.36. This result is gratifyingly close to the observed result between 50 and 55% sulfuric acid (slope of 0.3).

An alternate description may be formulated. This formulation specifically takes account of the fact that the relative concentrations of β -phenylcinnamic acid and of β,β -diphenyl- β -hydroxypropionic acid present in an equilibrium between the two are properly dependent on the activity of water in the solution. Such a more detailed formulation is more erudite and sophisticated, and correct. It leads to a different definition of some of the symbols and terms used. However it does not add anything to the primary conclusions or the general pattern of results to be expected. Hence it will not be presented in detail.

In summary, if the acidity of the solution is in the region (low acidity) where synchronous decarboxylation and dehydration is the dominant reaction of the hydroxy acid, then the behavior of the cinnamic acid will be characterized by a rate-determining hydration reaction followed by rapid decarboxylation–dehydration. On the other hand, if the acidity of the solution is such (very high acidity) that simple dehydration is the dominant reaction of the hydroxy acid, then the rate-limiting process will be the decarboxylation–dehydration of the very limited amount of hydroxy acid in equilibrium with the cinnamic acid.

N-Fluoroalkylamines. I. Difluoroazomethines

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Contribution No. 1093 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898. Received May 27, 1965

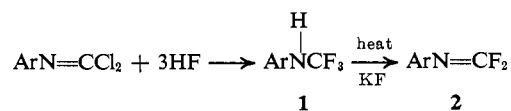
The reaction of isothiocyanates with mercuric fluoride provides a new general route to difluoroazomethines and is particularly useful for preparing N-aryldifluoroazomethines which are trapped as N-(trifluoromethyl)-N-(fluoroformyl)anilines by carbonyl fluoride addition. Exchange reactions of N-aryldichloroazomethines with metal fluorides are also described as routes to difluoroazomethines.

As part of a general study on the effect of fluorine substitution in organic molecules,² a synthetic program

(1) This work was presented in part at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964.

(2) (a) W. A. Sheppard, *J. Am. Chem. Soc.*, **84**, 3072 (1962); (b) W. A. Sheppard, *ibid.*, **85**, 1314 (1963).

was directed toward synthesis of N,N-bis(trifluoromethyl)anilines. Although a number of N-fluoroalkylamines are known³ and N-(trifluoromethyl)aniline (**1**, Ar = C₆H₅) has been reported from reaction of N-phenyldichloroazomethine with hydrogen fluoride,⁴



(3) (a) A. M. Lovelace, D. A. Rausch, and W. Postelnek, "Aliphatic Fluorine Compounds," Reinhold Publishing Corp., New York, N. Y., 1958, Chapters X and XI; (b) M. Hudlicky, "Chemistry of Organic Fluorine Compounds," The MacMillan Co., New York, N. Y., 1962.

(4) (a) K. A. Petrov and A. A. Neimysheva, *J. Gen. Chem. USSR* (Eng. Transl.), **29**, 2135, 2662 (1960); (b) E. Klauke and E. Kühle, German Patent 1,170,414 (1964).

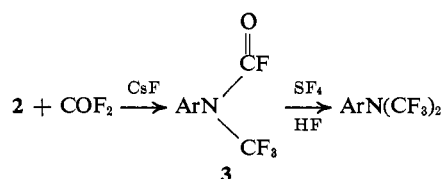
Table I. N-(Trifluoromethyl)-N-(fluoroformyl)anilines. Preparation from ArNCS, HgF₂, COF₂, and CsF, and Properties

XC ₆ H ₄ N- (COF)(CF ₃) substituent	B.p., ^a °C. (mm.)	M.p., °C., ^a or n _D ²⁰	Yield, %	Formula	Anal.								
					Carbon ^b		Hydrogen		Fluorine		Other		
					Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	
H	134 (180)	1.4293	77, 44 ^c	C ₈ H ₅ F ₄ NO	36.7	36.8	N,	6.8	6.8
F	meta 112 (122)	1.4191	45	C ₈ H ₄ F ₅ NO	42.7	43.1	1.79	2.03	42.2	42.4	N,	6.2	6.4
	para 128 (200)	1.4181	73		42.7	43.4	1.79	1.94	42.2	41.9	N,	6.2	6.5
Br	meta 144 (108)	1.4734	83	C ₈ H ₄ BrF ₄ NO	33.6	34.3	1.41	1.63	26.6	26.2	Br,	27.9	27.3
	para 130 (52)	1.4758	77		33.6	34.1	1.41	1.63	26.6	26.8	Br,	27.9	27.5
NO ₂	meta 90 (1.2)	49.2-50.4	71	C ₈ H ₄ F ₄ N ₂ O ₃	38.1	38.9	1.60	1.91	30.2	30.3	N,	11.1	11.4
	para 112 (3.2)	69.4-71.2	45		38.1	38.9	1.60	1.71	30.2	30.0	N,	11.1	11.2
CH ₃	meta 137 (170)	1.4352	53	C ₉ H ₇ F ₄ NO	48.9	49.2	3.19	3.38	34.4	34.2	N,	6.3	6.4
	para 105-106 (50)	1.4350	d		48.9	49.3	3.19	3.29	34.4	34.7	N,	6.3	6.7
OCH ₃	meta 148 (80)	1.4499	43	C ₉ H ₇ F ₄ NO ₂	32.1	31.5	N,	5.9	6.2

^a Boiling points and melting points are uncorrected. ^b Carbon analysis on compounds containing fluorine are often 0.4 to 0.7% high, although not reproducibly so. ^c Cesium fluoride omitted. ^d Prepared from reaction of *p*-CH₃C₆H₄N(COF)₂ with SF₄; see ref. 7.

no N,N-bis(trifluoromethyl)anilines have been described.

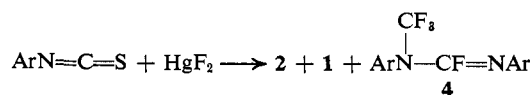
N-(Trifluoromethyl)-N-(fluoroformyl)anilines (**3**), potentially available by carbonyl fluoride addition to N-aryldifluoroazomethines (**2**), were chosen as suitable intermediates to react with sulfur tetrafluoride^{6,7};



thus a program to prepare N-aryldifluoroazomethines was undertaken. After the initial study was completed, the preparation of N-phenyldifluoroazomethine from N-phenyldichloroazomethine and hydrogen fluoride followed by hydrogen fluoride elimination with potassium fluoride^{4a} was described.

Results and Discussion

The reaction of mercuric fluoride with alkyl and aryl isothiocyanates is a general method for preparation of difluoroazomethines. When mercuric fluoride and an aryl isothiocyanate are heated in glass equipment and



the product is distilled or extracted into a solvent, the aniline **1** and the dimer **4** are also isolated. The aniline **1** must arise from hydrogen fluoride (from reaction of mercuric fluoride or the difluoroazomethine with glass) addition to **2**. A linear structure (**4**) is proposed for the dimer⁸ based on F¹⁹ n.m.r. analysis (doublet and quadruplet in intensity ratio of 3:1) and infrared spectra. This dimer probably forms by fluoride ion catalyzed condensation analogous to the carbonyl

(5) F. S. Fawcett, C. W. Tullock, and D. D. Coffman, *J. Am. Chem. Soc.*, **84**, 4275 (1962), reported the fluoride ion catalyzed addition of carbonyl fluoride to pentafluoro-2-azapropene to give N,N-bis(trifluoromethyl)carbonyl fluoride.

(6) (a) W. R. Hasek, W. C. Smith, and V. A. Engelhardt, *ibid.*, **82**, 543 (1960); (b) R. J. Harder and W. C. Smith, *ibid.*, **83**, 3422 (1961).

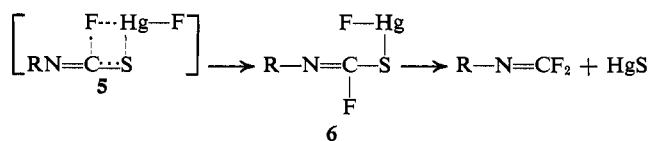
(7) The preparation and properties of N,N-bis(trifluoromethyl)anilines are described in paper II of this series: F. S. Fawcett and W. A. Sheppard, *ibid.*, **87**, 4341 (1965).

(8) In ref. 4a, a dimer of N-phenyldifluoroazomethine was reported as a by-product in the reaction of N-(trifluoromethyl)aniline with potassium fluoride, but no structure was proposed.

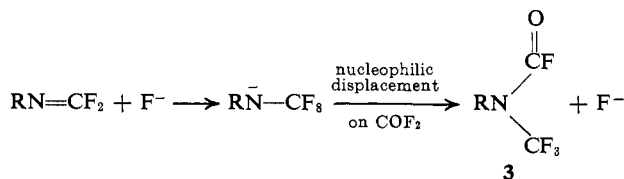
fluoride addition to olefins^{5,9} and is obtained in higher yields by extended heating of the reaction mixture. In the aliphatic series, N-ethyldifluoroazomethine was prepared from ethyl isothiocyanate in 37% yield, and no by-products were detected.

The N-aryldifluoroazomethines are difficult to handle in glass equipment (etching of equipment, contamination by anilines **1**) but were trapped directly with carbonyl fluoride to give N-(fluoroformyl)-N-(trifluoromethyl)anilines (**3**) in high yields. In these experiments, the mercuric fluoride, aryl isothiocyanate, carbonyl fluoride, and cesium fluoride were charged into a pressure vessel and gradually heated to 200°; aniline **3**, extracted and distilled, was obtained in yields of 45–83% with no significant amount of by-products (see Table I). A range of aromatic substituents (nitro, methyl, halogen) was used, and the method appears to be general for the majority of aryl groups which contain no active hydrogen. *p*-Methoxyphenyl isothiocyanate did however give an impure product, possibly from attack of the reagents on the methoxy group.

The mechanism of the reaction of mercuric difluoride with isothiocyanates was not investigated but is suggested to go by way of a four-center-type transition state **5** leading to an intermediate such as **6** which can



decompose to the azomethine and mercuric sulfide. The fluoride ion catalyzed addition reaction of carbonyl fluoride to olefins has been discussed,^{5,9} and the proposed mechanism is shown. Cesium fluoride provides



an excellent source of fluoride ions. Mercuric fluoride or some other species in the reaction can also function as a catalyst, but the yield of aniline **3** dropped from 77 to 44% when cesium fluoride was omitted.

(9) C. W. Tullock, D. D. Coffman, and E. L. Muetterties, *J. Am. Chem. Soc.*, **86**, 357 (1964), have reported the same type linear dimer from SF₄N=CF₂.

Table II. Reaction of N-Aryldichloroazomethine with Fluorinating Agents

X of $\text{XC}_6\text{H}_4\text{N}=\text{CCl}_2$	Amount, g.	Fluorinating agents, g.	Conditions	Products	Yields
H	35	NaF, 25	Heated at 160° in tetramethylene sulfone	Recovered starting material	<i>a</i>
H	43	KF, 35	Heated from 150 to 250° for 8 hr. in pressure vessel	$\text{C}_6\text{H}_5\text{N}=\text{CF}_2$	Trace ^a
H	17	AgF, 28	Heated at 160° overnight in Teflon ^b bottle	$\text{C}_6\text{H}_5\text{N}=\text{CF}_2$	25 to 50% ^a
H	26	CsF, 2 COF ₂ , 22	Heated at 200 to 280° over 10 hr. in pressure vessel	$\text{C}_6\text{H}_5\text{N}(\text{COF})(\text{CF}_3)$ $\text{C}_6\text{H}_5\text{N}=\text{CCl}_2$	13.8 g. (44%) 5.7 g.
H	35	KF, 31 COF ₂ , 25	Heated at 200 to 250° for 8 hr. in pressure vessel	$\text{C}_6\text{H}_5\text{N}(\text{COF})(\text{CF}_3)$ $\text{C}_6\text{H}_5\text{N}=\text{CF}_2$ $\text{C}_6\text{H}_5\text{N}=\text{CCl}_2$	10.8 g. 16.2 g.
<i>m</i> -NO ₂	33	CsF, 50 COF ₂ , 30	Heated at 200 to 275° over 8 hr. in pressure vessel	<i>m</i> -O ₂ NC ₆ H ₄ N(COF)(CF ₃)	12 g. (31%)

^a Products characterized by spectral analysis (F¹⁹ n.m.r. and infrared) only. ^b DuPont trademark for tetrafluoroethylene resin.

As an alternative route to N-aryldifluoroazomethines, metal fluoride metathetical reactions with N-aryldichloroazomethines were also studied. In preliminary experiments, N-phenyldichloroazomethine was shown by F¹⁹ n.m.r. analysis to give the difluoroazomethine with silver monofluoride, cesium fluoride, or potassium fluoride, by heating, both with and without solvent. Again quantitative experiments were run using the carbonyl fluoride trapping technique. The results are summarized in Table II; cesium fluoride appeared to be the best reagent for this reaction, and aniline **3** was obtained from N-phenyl- or N-(*m*-nitrophenyl)-dichloroazomethines in yields of 44 and 31%, respectively.

N-(Fluoroformyl)-N-(trifluoromethyl)aniline was treated with dimethylamine to give the corresponding urea. The reaction of anilines **3** with sulfur tetrafluoride to give the N,N-bis(trifluoromethyl)anilines is described in the next paper.⁷

Experimental Section

Materials. The isothiocyanates and other normal reagents were obtained from chemical supply houses such as Eastman Kodak or prepared by standard literature procedures.¹⁰ The mercuric fluoride was supplied by Harshaw Chemical Corp.

1. Reaction of Isothiocyanates with Mercuric Fluoride. *A. Aryl Isothiocyanates.* Phenyl isothiocyanate (27.0 g., 0.20 mole) was placed in a 100-ml., three-necked flask fitted with a true-bore stirrer with vacuum-tight bearing, thermometer, solid addition funnel, and distillation head. The exit from the distillation column was connected in series to a Dry Ice trap and vacuum pump. After the reaction pot was heated to 100° and the pressure was reduced to 50 mm., 96 g. (0.40 mole) of mercuric fluoride was added portionwise from the solid addition funnel as the reaction temperature was gradually raised to 150°. The pressure was reduced to 25 mm. and the volatile products (16.5 g.) were collected in the receiver and Dry Ice trap. The residual yellow solid in the pot was extracted with chloroform. On evaporation of this chloroform extract, an additional 8.8 g. of solid and liquid was obtained. The combined products were distilled to give

the following main fractions: A, 4.8 g., b.p. 58° (53 mm.); B, 3.82 g., b.p. 64–86° (62 to 10 mm.); C, 8.7 g., b.p. 86° (10 mm.); and D, 2.6 g., b.p. 89–94° (1 mm.). Fraction A was identified as N-phenyldifluoroazomethine, yield 17% (lit.^{4a} b.p. 55–57° at 17 mm.) by infrared analysis (N=C at 1785 cm.⁻¹) and n.m.r., both proton (only aromatic CH) and F¹⁹ (at room temperature, very broad peaks centered approximately at +50.4 and +58.2 p.p.m. in CCl₃F as calibrant and solvent; at 76°, single broad peak at 54.4 p.p.m.; at -60°, two sets of doublets centered at +49.0 and +57.5 p.p.m., with *J* = 50 c.p.s.).

Anal. Calcd. for C₇H₅F₂N: C, 59.6; H, 3.57; F, 26.9; N, 9.9. Found: C, 60.0; H, 3.96; F, 27.0; N, 10.8.

Fraction B was characterized as impure N-(trifluoromethyl)aniline (lit.^{4a} b.p. 52° at 12 mm., NH in both infrared and proton n.m.r., F¹⁹ n.m.r., doublet at +56.6 p.p.m. in CCl₃F as calibrant and solvent, *J* = 5.4 c.p.s.) containing some N-phenyldifluoroazomethine (yield approximately 12%). Fraction D was characterized as a linear dimer of N-phenyldifluoroazomethine, yield 11%, *n*^{25D} 1.5206 (lit.^{4a} b.p. 128–129 at 2.5 mm., *n*^{25D} 1.5208).

Anal. Calcd. for C₁₄H₁₀F₂N₂: C, 59.6; H, 3.57; N, 9.9. Found: C, 59.9; H, 4.15; N, 9.8.

The linear dimer structure was proved by infrared (C=N at 1740 cm.⁻¹) and n.m.r., F¹⁹ doublet (intensity 3) +56.2 p.p.m., quadruplet (intensity 1) at +50.9 p.p.m., *J* = 15 c.p.s. (in CCl₃F as internal calibrant and solvent) and proton only aromatic hydrogen.

By running the reaction in a stainless steel pressure vessel and heating at 100° for 2 hr. and at 130 and 150° for 4 hr. each, the yield of dimer increased to 62% but the yields of N-phenyldifluoroazomethane and recovered phenyl isothiocyanate dropped to 7 and 6%, respectively.

p-Chloro- and *m*-nitrophenyl isothiocyanates were also shown to react with mercuric fluoride in a similar manner to phenyl isothiocyanate, but the products were characterized by F¹⁹ n.m.r. only.

B. Ethyl Isothiocyanate. Ethyl isothiocyanate (15.0 g., 0.173 mole) was added dropwise to 96 g. (0.4 mole) of mercuric fluoride heated at 100° in equipment similar to that described above. The volatile product collected in the Dry Ice trap was distilled (4.3 g., 37%

(10) G. M. Dyson, "Organic Syntheses," Coll. Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1951, p. 165.

yield), b.p. 17–18° and was characterized as N-ethyl-difluoroazomethine.

Anal. Calcd. for C₃H₅F₂N: F, 40.8. Found: F, 40.5, 40.3.

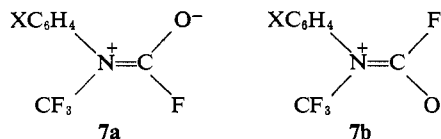
Spectral characterization was n.m.r., F¹⁹ doublets at –10.96 and –10.86 p.p.m. relative to external trifluoroacetic acid (approximately +65.6 and 65.7 relative to CCl₃F); proton, typical ethyl; mass spectrum showed pattern expected for C₂H₅N=CF₂. A total of 34% of unreacted ethyl isothiocyanate was recovered and no by-products were detected.

2. *Reaction of Isothiocyanates with Mercuric Fluoride and Carbonyl Fluoride.* A mixture of 27.0 g. (0.20 mole) of phenyl isothiocyanate, 96 g. (0.40 mole) of mercuric fluoride, and 10 g. of cesium fluoride was charged into a 240-ml. stainless steel pressure vessel. The vessel was chilled, evacuated, charged with 25 g. (0.38 mole) of carbonyl fluoride,⁵ and then heated for 2-hr. intervals successively at 60, 100, 140, 175, and 200°. The crude product (light-colored solid) was extracted with several portions of methylene chloride. The combined extracts were distilled to give 31.7 g. (77%) of N-(fluoroformyl)-N-(trifluoromethyl)aniline, b.p. 134° (180 mm.).

A series of aryl isothiocyanates was run in a similar manner and the yields, physical properties, and analytical data are given in Table I.

N-(Fluoroformyl)-N-(trifluoromethyl)-*m*-fluoroaniline, typical of the series, had the expected F¹⁹ n.m.r. pattern (10% in CCl₃F as solvent and internal calibrant) of CF₃ doublet (intensity 3) at +56.8 p.p.m. and COF quadruplet (intensity 1) at +4.04 p.p.m., *J* = 15 c.p.s. On chilling, the pattern broadened and resolved at approximately –30° into two sets of doublets and quadruplets of unequal intensity. The result is readily explained by restricted rotation¹¹ resulting from increased contributions from forms such

as 7. Correlation studies on the effect of substituent



X with barrier and chemical shifts are currently in progress with Dr. D. R. Eaton of this laboratory.

Infrared, ultraviolet, and proton n.m.r. spectra were also obtained on these anilines. The carbonyl frequency was in the region of 1835 cm.⁻¹.

3. *Reaction of N-Aryldichloroazomethines with Metal Fluorides.* A series of metal fluoride exchange reactions with N-aryldichloroazomethine was carried out. The experimental conditions and results are given in Table II. Trapping of the azomethine product directly with carbonyl fluoride was found best in these reactions.

4. *Reaction of N-(Fluoroformyl)-N-(trifluoromethyl)aniline with Diethylamine.* Excess anhydrous diethylamine was bubbled into a solution of 8.43 g. (0.0408 mole) of N-(fluoroformyl)-N-(trifluoromethyl)aniline in 150 ml. of ether. The reaction was exothermic, and a white precipitate was removed by suction filtration after the reaction was over. The filtrate was distilled to give 7.04 g. (75%) of N-phenyl-N-(trifluoromethyl)-N',N'-dimethylurea, b.p. 111° (3.2 mm.), *n*_D²⁰ 1.4760.

Anal. Calcd. for C₁₀H₁₁F₃N₂O: F, 24.6; N, 12.1. Found: F, 24.2; N, 11.8.

Only a single resonance at –10.1 p.p.m. (relative to CF₃CO₂H) was seen in the F¹⁹ n.m.r. spectrum. Infrared and ultraviolet spectra were as expected.

(11) W. D. Phillips in "Determination of Organic Structures by Physical Methods," Vol. 2, F. C. Nachod and W. D. Phillips, Ed., Academic Press Inc., New York, N. Y., 1962, p. 441. The N-(fluoroformyl)anilines are analogous to formamides.

N-Fluoroalkylamines. II. N,N-Bis(trifluoromethyl)anilines

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Contribution No. 1094 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898. Received May 27, 1965

N,N-Bis(trifluoromethyl)anilines, a new class of compounds, have been prepared by reaction of *N*-(fluoroformyl)-*N*-(trifluoromethyl)anilines with sulfur tetrafluoride. The physical and chemical properties of this class of compounds are described. The inductive and resonance effects of the *N,N*-bis(trifluoromethyl)amino group are reported in comparison to other fluorinated substituents and discussed in terms of current theories of origin and transmission of inductive and resonance effects.

N,N-Bis(trifluoromethyl)anilines (1) have not been reported in the literature, although a number of fluoroalkylamines are known² and recently *N*-(trifluoro-

(1) This work was presented in part at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964.

methyl)aniline was described.³ The electronic effects of the bis(trifluoromethyl)amino group were of particular interest for comparison to other fluorinated substituents such as CF₃, OCF₃, SCF₃, and SF₅.⁴ In the preceding paper,⁵ *N*-(fluoroformyl)-*N*-(trifluoromethyl)anilines (2) were described as precursors to anilines 1.

(2) (a) A. M. Lovelace, D. A. Rausch, and W. Postelnek, "Aliphatic Fluorine Compounds," Reinhold Publishing Corp., New York, N. Y., 1958, Chapters X and XI; (b) M. Hudlicky, "Chemistry of Organic Fluorine Compounds," The MacMillan Co., New York, N. Y., 1962.

(3) (a) K. A. Petrov and A. A. Neimysheva, *J. Gen. Chem. USSR* (Eng. Transl.), **29**, 2135, 2662 (1960); (b) *N*-(difluoromethyl)-*m*-methoxyaniline and *N,N*-bis(difluoromethyl)-*m*-toluidine were reported to have been prepared from reaction of the aniline with a difluoromethyl halide (HCF₂X): J. B. Dickey, U. S. Patent 2,516,302 (1950).

(4) W. A. Sheppard, *J. Am. Chem. Soc.*, **85**, 1314 (1963); **84**, 3072 (1962).

(5) W. A. Sheppard, *ibid.*, **87**, 4338 (1965).